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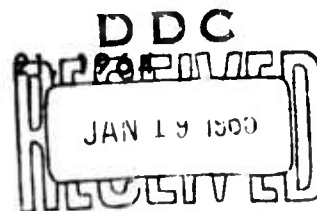
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DEPARTMENT

BASIC STUDY OF SORPTION OF ORGANIC FUELS DURING OXIDATION AT ELECTRODES

FINAL REPORT

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BASIC STUDY OF SORPTION OF ORGANIC

FUELS DURING OXIDATION AT ELECTRODES

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FOREWORD

This is the final progress report prepared by the Research and Development Department of the American Oil Company under Contract No. DA-11-022-ORD-4023; ARPA Order No. 247-62, Amdt. 4, Task 5. The research reported is a part of the Energy Conversion Project sponsored by the Advanced Research Projects Agency, Department of Defense. The AROD Project Number is 3472. This report covers work done from Sept. 13, 1961 to October 21, 1964, and includes previously unreported work for the twelfth quarter, July 1, 1964 to October 21, 1964.

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ABSTRACT

The objective of this program was an improved understanding of the role of sorption processes at electrodes in the electrochemical oxidation of carbonaceous fuels with special emphasis on the development of novel experimental approaches to this end. Of the many techniques studied, the radiolabeled sorption, differential capacitance, voltage step and potential sweep techniques were found to be the most useful for studies of selected light hydrocarbon, methanol and formic acid fuels.

For the radiolabeled sorption technique, the most difficult development problem was achieving an adherent, 2000 Å-thick platinum film-electrode on a thin (6 mil), mica substrate through which the activity of the radiolabeled fuel is measured. This problem was solved by using a graded Ta oxide -Ta layer between the mica and the platinum. First applications showed that adsorption of n-butane on Pt at 25°C from 1N H_2SO_4 is a function of potential with peak adsorption occurring at about +0.3V (NHE). Adsorption and desorption are slow, requiring 2-8 hours for equilibrium. The tool can be applied to direct studies of adsorption of fuel at fuel electrodes as functions of composition, concentration and structure of fuels, electrolytes, and electrodes with reference to effects of electrode potential and temperature.

Differential capacitance studies of methanol and formic acid fuels on Pt in 1M H_2SO_4 at temperatures less than 80°C reveal strong, activated adsorption of Temkin form with rates following Elovich behavior. Studies of propylene in 1M H_2SO_4 at 80°C and propane in 85% H_3PO_4 at

140°C revealed adsorption at these but not lower temperatures. Because of low solubilities, isotherms were not obtained.

Electrooxidation studies with methanol, formic acid and ethylene in 1M H_2SO_4 at 25°C showed easier oxidation at a freshly reduced platinum surface. Potential sweep studies showed oxidation at potentials where no surface oxide was present with peak heights increasing in the order: propane, ethane, butene, propylene, ethylene.

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INTRODUCTION

This is the Final Report issued under Contract No. DA-11-022-ORD-4023, ARPA Order No. 247-62, Amdt. 4, Task 5, titled "Basic Study of Sorption of Organic Fuels During Oxidation at Electrodes." The research reported was carried out at the Whiting (Ind.) Research Laboratories of the American Oil Company during the period Sept. 13, 1961 to October 21, 1964. This report was prepared by the Research and Development Department of the American Oil Company.

The program had as its objective an improved understanding of the role of sorption processes in electrochemical oxidation of fuels with special emphasis on the development of novel experimental approaches to this end. Eight approaches were applied to the problem:

1. Studies of the sorption of radiolabeled fuels on metal films at a thin-window Geiger counter.

2. Studies seeking detection of free-radical intermediates at electrodes using electron-spin-resonance measurements.

3. Application of novel infrared techniques in attempts to characterize bonding at electrodes.

4. Double-pulse studies of electrode polarization.

5. Studies of sorption effects at electrodes by the differential capacitance method.

6. X-Y pulsed polarization studies of fuel electrodes.

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7. Chronopotentiometric studies of sorbed fuels.

8. Studies of the effects of in situ irradiation on fuel electrodes.

This report summarizes the work of the entire contract and includes new work for the twelfth (final) quarter of the contract. Work in the twelfth quarter was concentrated in the radiolabeled sorption area.

During this project the radiolabeled sorption technique was developed into a generally useful tool for fuel cell studies with broad potential scope of application. Differential capacitance and certain methods of study of electrooxidation were found useful with methanol and selected hydrocarbon fuels. The infrared, electron-spin-resonance, double-pulse and X-Y pulsed polarization techniques were found not to be useful methods.

Application of the radiolabeled sorption technique to fuel electrode problems is being carried out under a new contract, Contract DA-49-186-AMC-167(X).

SORPTION OF RADIOLABELED FUELS

The objective of this portion of the research was the direct measurement of sorption of fuels from aqueous electrolytes onto thin metal films under electrochemical control using radiolabeled fuels and a thin-window proportional counter. Most of the work during the project centered on the development of apparatus and technique for platinum film-electrodes with methanol and n-butane fuels. The apparatus and technique were perfected during the project and the application to studies of the n-butane at sputtered platinum in sulfuric acid electrolyte was initiated. Of the several novel techniques explored as possibly being adaptable for application to studies of the role of sorption processes in the fuel electrode reaction, this is the only one which was capable of successful application. The resulting technique is broad in scope of potential application. It can be used for study of the effects on fuel adsorption and fuel oxidation of fuel composition, structure, and concentration, electrolyte composition and concentration, electrode composition and structure, electrode poisons, electrode potential and temperature.

Description of Technique

The technique was based upon one developed earlier in this laboratory[1,2] which measures directly and continuously the adsorption of C^{14} labeled, non-volatile, polar compounds from non-aqueous media onto

metal films, vapor-deposited in high vacuum. The metal film is deposited
onto a suitable substrate, such as mica, and both are thin enough to
permit passage of C^{14} beta radiation (cf. diagram in Figure 1). The total
counting rate measured by the counter is that for a thin layer of the
solution adjacent to and in contact with the metal film plus that for any
radiolabeled compound adsorbed on the surface of the metal film. For
fuel cell studies the thin metal film is made of electrocatalytic mate-
rial (Pt) and is made an anode by electrical contact. The fuel is radio-
labeled fuel dissolved in typical aqueous electrolytes, such as H_2SO_4 or
KOH. The amount of adsorption, after a given time interval, is deter-
mined by subtracting the count of the solution from the total count.

Adaptation to Fuel Cell Studies

The application of this technique to fuel cell studies involved
many extensive changes in both design of apparatus and procedure from
those used in the earlier work. The adsorption cell had to be redesigned
to accommodate volatile fuels and less volatile, but corrosive, elec-
trolytes. It had to be functional electrochemically and be made of mate-
rials that would not absorb and deplete the electrolyte of fuel. The
electrode window had to meet a number of rigid requirements discussed
below.

Two practical and highly sensitive adsorption cells were developed, one with an internal counter electrode and the other with an external counter electrode and magnetic stirring. Components of these cells and techniques evolved simultaneously through several stages of development. The final cell (two versions) and the solutions of problems leading to it are described below. Pertinent adsorption data obtained so far on two fuels and three electrolytes are also given.

Window Electrode

The window electrode had to be (1) thin enough to pass weak C^{14} beta radiation, (2) unaffected by aqueous electrolyte, at all anodic potentials of interest, (3) thick enough for low electrical resistance, (4) of composition pertinent to fuel electrode studies, and (5) firmly adherent to the window material in the presence of electrolyte at the potentials used. Thin foils of pure metal such as have been used by other workers[3,4,5] were not used in this work because of low penetrability by C^{14} beta radiation. It is extremely difficult to obtain a pin-hole free, 3000-4000 Å-thick metal foil (which would pass enough radiation) of sufficient size. Pin-hole free foils 20,000 Å thick are obtainable but result in too high absorption of β radiation. Such foils would necessitate the use of a fuel of high specific activity, which greatly reduces the sensitivity of the measurements, by diminishing the excess of count

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due to adsorbed fuel over the solution count, and greatly increases the cost of each experiment. Foils have a roughness factor of only about 1.5 and this results in decreased adsorption sensitivity because the difference (due to adsorption) between the overall counting rate and the counting rate of the solution is relatively small.

For these reasons, electrode-windows were prepared by vapor-depositing the metal onto a suitable window substrate. Mica is ideal because it can be obtained thin enough to pass most of the beta radiation, it can withstand temperatures up to 650°C without exfoliating, and it does not react with or adsorb the fuel or electrolyte because of its smooth low-energy surface and nonporous structure. Windows made of thin Mylar or Teflon could be used with such fuels as methanol, but they could not be used with light hydrocarbons (such as n-butane) because of their permeability to these gases.

Platinum film-electrodes were used in all experiments. Sufficiently thick film could not be deposited by evaporation in high vacuum because of their extremely slow evaporation from a platinum filament, or because of contamination or alloying with tungsten from a tungsten filament. Good films were prepared by physical sputtering of platinum at a low pressure of argon (0.05 Torr).

The thickness of the platinum films was determined by calculation from weight gain assuming bulk density for the platinum (the films are actually thicker because of their porosity). Weight gain during sputtering was found to be linear with sputtering time as shown in Table I and Figure 2. Sputtering time was therefore used to control electrode thickness. The absorption of beta radiation is also linear with sputtering time (hence, also electrode thickness). Corrections for beta losses through the electrode were made based on sputtering time.

TABLE I

PROPERTIES OF SPUTTERED PLATINUM FILMS

Voltage: 1025 VDC, Current: 5.0 ma, Argon pressure: 0.05-0.11 Torr

Minutes Sputtered	Calculated Film Thickness Å	% Beta Radiation Absorbed
5	360	3.91
10	630	7.60
15	940	11.98
20	1280	16.68
32	2000	25.7

To obtain sufficient electronic conductivity through the electrode, 2000 Å-thick films were required. A 2000 Å-thick film was deposited by sputtering 32 minutes at 1025 volts and 5 ma. The films are porous and appear to have a roughness factor as high as 30, which greatly increases

the sensitivity of detection of adsorption.

Although the properties of inertness, nonporosity, and smoothness were desirable in mica for the previously mentioned reasons, they were the cause of the troublesome problem of the lack of adhesion of the sputtered platinum film to the mica. This is no problem when nonaqueous solutions are used, but when the film was contacted with water and especially aqueous ionic electrolytes, it was readily stripped from the mica. This problem becomes even more severe with prolonged contact with the electrolyte and electrode potential cycling (alternate oxidation and reduction) in which electrode currents are in excess of a few milliamps.

Many different techniques were tried in solving this problem, including etching or roughening of the mica, various annealing techniques, application of underlayment films beneath the platinum, and combinations of these. The use of underlayment films appeared to be the best approach, but it was necessary for the underlayment film not to affect the electrochemical properties of the platinum, or be affected by the electrolyte, fuel, or potential cycling of the electrode. The problem was solved by using tantalum, which meets all of these qualifications. A graded tantalum oxide-tantalum film was used because the oxide adheres much more strongly to mica. Tantalum has been made to adhere to quartz in thin-film capacitor studies by a similar technique.[6,7] Adherence of the oxide

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to the tantalum and the tantalum to the platinum is also good. The thin
(50-200 Å) underlayment film is first applied to the mica by sputtering
15 minutes at 2200 volts and 10 ma. For the first 2 minutes, the tan-
talum is reactively sputtered in dry air to deposit the oxide. The gas
is then changed to argon for the remaining 13 minutes to deposit pure
tantalum. The underlayment film is protected from atmospheric air with
a blanket of argon while the apparatus is dismantled and the tantalum disk
is replaced with one of platinum. The 2000 Å-thick platinum film is then
sputtered as usual. If properly prepared, the window-electrode will with-
stand repeated potential cycling, prolonged contact with the electrolyte,
and electrode currents in excess of 10 ma.

A support for the window was necessary in order to prevent
breakage and to provide external electrical contact with the platinum
film. Clamping of the window between metal or Teflon rings resulted in
window breakage. Mounting the window in a metal ring with epoxy resin
was satisfactory except that certain electrolytes reacted with the resin.
The best mounting was obtained by sealing the mica window between two
metal rings with Pyroceram #95 Solder Glass (Corning), as shown in
Figure 3. The upper ring was milled from platinum so that it would not
be affected by the electrolyte. The lower ring was made of an alloy of
48.5% nickel and 51.5% iron. The coefficients of expansion of the plati-

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num, mica, and Pyroceram are identical. That of the alloy is slightly less so that the mica would be taut after sealing the window. Sealing is done by heating the assembly to $450^{\circ}C$, at which temperature the Pyroceram vitrifies into glass.

The metal films are sputtered after mounting the window so that electrical contact is made between the platinum film and the platinum ring. For a 2000 Å-thick platinum film, the electrical resistance from the ring to a small drop of mercury placed in the center of the window is about 1 ohm. Electrical contact is made around the entire perimeter of the window. For a current of 1 milliamp the potential difference, center to edge, would be somewhat less than 1 millivolt, hence the film-electrode is essentially equipotential and the current density is uniform.

Adsorption Cells

Several cell designs were tested and it was found that construction materials were essentially limited to platinum, glass, and thin coatings of Teflon. Plastics, including solid Teflon, and other metals could not be used because the materials either absorbed and depleted the electrolyte of light hydrocarbon fuels (such as n-butane), or reacted with the acid or base electrolyte. Another requirement was that the cell be easy to dismantle and clean. The final cell that met

the necessary requirements is shown in Figure 4. The counter electrode is a solid platinum disk silver-soldered in the bottom of a stainless steel cup. The sides of the cup are protected from the electrolyte with a coating of FEP Teflon. This thin coating of Teflon apparently absorbs very little of the fuel, and it also serves as electrical insulation between the cup and the ring-window assembly. The ring-window assembly is sealed to the cup with wax so that the cell can be easily dismantled. The wax is applied from the outside and no wax gets inside the cell. Figure 5 shows the cell with the inlet and outlet tubes and a reference electrode. The cell is filled bubble-free with a hypodermic syringe equipped with a standard-taper glass fitting instead of the usual Luer taper. The cell is filled at the standard-taper joint where the reference cell is normally connected. The outlet capillary tube is left open to release any pressure that might develop in the cell and rupture the delicate window. Small amounts of volatile fuels are lost through the outlet tube, but the rate is slow (diffusion) and reproducible.

Another cell was developed so that an external counter electrode and magnetic stirring could be used. The external counter electrode is advantageous because any fuel adsorption, loss of fuel from the solution, or formation of fuel reaction products at the counter electrode is less likely to affect the adsorption on the cell-window working elec-

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trode. Magnetic stirring is necessary for studies of adsorption kinetics. As shown in Figure 6, the cell is made mainly of Pyrex glass. The counter electrode is a roll of platinum gauze, and any pressure developed within the cell is released through the capillary tube leading to the electrode. This cell is also mounted vertically against the proportional counter tube and the magnetic stirring bar is rotated at 100 RPM in the vertical plane. Vertical orientation is preferred to prevent blockage of portions of the window-electrode by gas bubbles remaining when the cell is filled or after gas evolution.

Preparation of Cell for Adsorption Measurements

The following procedure for preparing the cells for adsorption measurement was adopted to provide for exclusion of oxygen and preconditioning of the electrode. Oxygen must be rigorously excluded to prevent its direct reaction with the fuel at the catalytically active platinum electrode. Such oxidation might 1) deplete the fuel, 2) alter the adsorption characteristics of the electrode surface, or 3) generate products of different and dominant adsorption behavior. Because the state of the electrode surface is likely to be important in determining its adsorption behavior and because conditioning of the electrode (e.g., by potential cycling) can produce undesirable products such as oxygen or partial oxidation products in the electrolyte, the electrode was pre-

conditioned in fuel-free electrolyte. The following procedure was usually followed.

The cell was purged with purified argon and filled with deaerated electrolyte. The window-electrode potential was then adjusted to the desired value with a Wenking potentiostat. After the cell current decreased to zero or reached equilibrium, the cell was emptied by inverting it and applying a slight argon pressure at the standard-taper joint. The cell was then refilled with deaerated, radiolabeled, fuel-electrolyte solution, the electrode potential was readjusted to the desired value, and counting was started. Care was taken at all times to prevent air from entering either the cell or the solutions.

Preparation of Radiolabeled Solutions

Two fuels have been studied, radiomethanol and radio n-butane, having specific activities between 1 and 2 millicuries per millimole. Stock solutions of 0.00055 molal concentration were prepared by dissolving the materials in deionized redistilled water. Nine parts of stock solution mixed with one part of 1C N electrolyte gave the final solution of 1 N electrolyte containing a 0.0005 molal concentration of the fuel.

Because the stock solutions had to be devoid of dissolved oxygen or air and because of the high volatility of the fuel, a special apparatus was developed for preparation of the solutions, as shown in Figure 7. For

a given amount of radioactive fuel, the apparatus was constructed to have the exact volume required for a 0.00055 molal concentration. The main part of the apparatus was first evacuated to 10^{-8} Torr. The fuel was let into the vacuum, followed by deionized redistilled water that had been deaerated by boiling and purging with argon. If necessary, the solution was agitated and pressurized with argon to dissolve the fuel. Degassed redistilled mercury was used to displace the solution as it was withdrawn from the top by a hypodermic syringe.

The final solution put into the adsorption cell was prepared by first putting 1 cc. of deaerated 10 N electrolyte in a 10 cc. hypodermic syringe. The syringe, equipped with a standard-taper glass fitting, contained a glass bead and was previously purged with argon. Nine cc. of the stock solution was then withdrawn with the syringe, the solution was mixed with the glass bead by tilting the syringe back and forth, and the solution was injected into the argon-filled adsorption cell.

Calibration of the Adsorption Cell

The total counting rate measured by the proportional counter tube during an adsorption experiment is that for a layer of solution 0.3 mm. thick in contact with the window, i.e., the solution count, plus that for any radioactive fuel adsorbed on the surface of the metal film.

The thickness of the layer of solution which contributes to the count rate is determined by the following calculation.[8] Since the amount of radiation absorbed is a function of the density (g/cm^3), as well as the length of path (cm), the "range" can be given in units of weight per unit cross-section of path (mg/cm^2).

$$\text{Range } (mg/cm^2) = 412E_o^{1.265-0.0954 \ln E_o}$$

where E_o is the energy of the radiation in electron volts. For C^{14}, E_o is 0.16 Mev.

$$R = 412(0.16)^{1.265-(0.0954 \ln 0.16)}$$

$$= 29.43 \ mg/cm^2$$

The thickness of the layer penetrated, T, is R/d where d is the density of the medium. For water, d is 1000 mg/cm^3.

$$T = R/d = 29.43/1000 = 0.029 \ cm \cong 0.3 \ mm$$

The thickness of the layer penetrated is 0.3 mm. Only the activity in solution within 0.3 mm. of the window contributes to the solution count, the rest is self-absorbed in the solution.

The solution count was determined indirectly using a standard source[9] consisting of an epoxy resin disk that contained a 0.0005-molal concentration of radio-stearic acid. The acid was dissolved in the liquid resin which was then polymerized and molded into a disk large

enough to cover the mica window of the counter tube. To eliminate any effect of surface concentration, the disk was milled to half its original thickness. Neither milling nor varying the roughness of the milled surface changed the count of the disk. A weight basis for concentration (molal) was used so that the count would be independent of the density of the resin. A weight basis is necessary because the self-absorption of the resin or solution is a function of density, not volume.

The solution count of an electrolytic solution containing an identical concentration of radioactive fuel is the counting rate at the surface of the resin disk times the ratio of the specific activities of the fuel and radiostearic acid. Later it was found that neither methanol nor n-butane was adsorbed on mica and that the solution count could be determined directly by simply using an uncoated mica window on the adsorption cell. The solution counts obtained directly were identical with those obtained using the standard source.

It was necessary to calibrate each new window or window-electrode because the mica varied in thickness and, together with the metal films, reduced the total counting rate by 40-60%. The window was calibrated by first counting the surface of the disk and then counting the disk again through the window by placing the disk as close as possible without touching the surface of the mica or metal film. The resin disk

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was also used as a standard source to check the operation of the proportional counter. This was done immediately before each experiment by placing the disk directly on the counter tube, and the data was corrected for any change in the inherent counting characteristics of the apparatus so that data from all experiments might be compared directly. The background count, which varied from 18 to 24 counts per minute, (C/M), was subtracted from all counting rates. Back-scattering for the electrolytes was assumed to be the same as that for the epoxy resin.

The roughness factor of the platinum film, with respect to small molecules such as methanol or butane, was estimated to be about thirty, according to preliminary chronopotentiometric measurements. Adsorption of radiomethanol was reported as "apparent monolayers". The counting rate of an apparent monolayer was calculated from the specific activity, assuming hexagonal closepacking of the molecules standing on end, and a roughness factor of unity. Adsorption of radio n-butane was reported as counts/minute (over-all counting rate minus solution count) because the type of packing of butane molecules is not known. If a reliable technique for area measurement, such as cathodic stripping of oxide for platinum, were fully developed, adsorption could be reported as square angstroms of surface area occupied per molecule, or as actual monolayers assuming some scheme of molecular packing.

Adsorption of Radiomethanol

Some work was done with radiomethanol early in the project before the problems of the development of the technique were fully understood. The results were obtained in a cell of early design, shown in Figure 8. This cell design contained many of the features which subsequently were found unsuited to studies of volatile hydrocarbons, such as Teflon parts, Mylar windows, epoxy cement, a gas space in the cell, and no deaeration of solutions. The data obtained were amenable to qualitative interpretation and helped guide the development of the technique.

Radiomethanol (0.0005 molal solutions) was adsorbed at 25°C onto bare Mylar and onto 1000 Å-thick platinum films on Mylar from pure water and from 0.025 molal aqueous solutions of H_2SO_4 and KOH. Open circuit conditions were used; i.e., no potentials were applied to the cell. Mylar windows were used because this work was done before the mica-platinum adhesion problem was solved. Although Mylar absorbs butane, it does not absorb methanol and there is no platinum adhesion problem. Ten cc. of solution were used and there was an 18 cc. space above the solution filled with argon.

As shown in Figure 9, adsorption of radiomethanol from pure water reached a maximum of 10.5 apparent monolayers at 20 minutes. The adsorption then decreased to zero monolayers (solution count) after 5 hours.

From aqueous KOH, 11.8 apparent monolayers were adsorbed after 7 minutes. Adsorption then decreased very rapidly to zero monolayers (solution count) and remained at that value. From aqueous H_2SO_4, 10.5 apparent monolayers were adsorbed after 30 minutes. Adsorption decreased rapidly to zero at 1.4 hours, but the counting rate continued to decrease and approached closer to zero counting rate than it did with pure water.

The results were interpreted as follows: the radiomethanol was initially adsorbed onto the platinum to the same extent, 10 to 12 apparent monolayers, in acid, base, and neutral water. This would be about one-third of an actual monolayer if the roughness factor of the platinum film is 30. The fact that the amount of adsorbed activity decreased instead of remaining constant indicated that the adsorbed methanol was subsequently oxidized to $C^{14}O_2$ by the small amount of oxygen present in the solution. The carbon dioxide product was not adsorbed by the platinum and it desorbed as it was formed.

In the alkaline solution, the $C^{14}O_2$ formed carbonate ion and remained in the solution. The apparent monolayer count dropped to zero when all of the radiomethanol was converted to carbonate. Zero mono-layer count, i.e., solution count, represents distribution of the radio-activity throughout the solution with no specific adsorption.

In the acid solution, the $C^{14}O_2$ product was not soluble and it was rejected from the solution into the static argon space above. When all of the radiomethanol was converted to $C^{14}O_2$, no radioactivity remained in solution and the monolayer count dropped below zero to a value equivalent to zero counting rate. (The CO_2-free solution screened the counter from the radioactive gas phase.)

In pure water, the CO_2 was partially soluble and most of it escaped into the argon atmosphere above. There was an activity loss of 72% from the solution, which is in good agreement with the value of 70% calculated from Henry's Law for the 10 cc. solution volume and the 18 cc. argon volume in the adsorption cell.

The conversion of radiomethanol to $C^{14}O_2$, indicated by the results, could occur in two ways. Platinum is a known catalyst for the oxidation of methanol. For this mechanism, the oxygen and methanol must come together on the platinum surface. Platinum is also electrocatalytic for the oxygen and methanol electrodes. By local cell action, methanol and oxygen can react even if they are adsorbed at separate places on the electrode. Such local cell action would be dependent on the ionic conductivity of the solution, being more rapid in strong acid or base than in pure water. The results of the above experiments may reflect direct catalytic reaction of methanol and oxygen for all three solutions, aug-

mented by local cell oxidation of methanol in the strong acid and strong base cases. The "desorption", interpreted as oxidation of methanol, is five times slower in water than in acid or base.

Adsorption of Radio-n-butane

Radio-n-butane (0.0005 molal solutions) was adsorbed from 1N H_2SO_4 at 25°C onto 2000 A^2-thick tantalum-bonded platinum films. At this concentration, for these conditions, the solution is about 1/4 saturated in butane, i.e., saturation in 1N H_2SO_4 at 25°C is about 2 millimolar.[10-12]

For these experiments, potential control of the film electrode was introduced. The cell had either an external counter electrode (shown in Figure 6) or an internal counter electrode (cf. Figure 5), and a mercury-mercurous sulfate reference electrode. The potential of the window-electrode was controlled with a Wenking potentiostat.

Preliminary work (cf. Figure 10), using the internal counter electrode cell and no tantalum underlayment film, had shown that butane is reversibly adsorbed at potentials between -0.2 and -0.5V relative to the Saturated Mercurous Sulfate electrode ($Hg/Hg_2SO_4/1N H_2SO_4$ + Sat'd Hg_2SO_4). Maximum adsorption occurred at about -0.25 volts (SMSE) when the electrode potential was changed stepwise in the anodic direction. When the potential was changed back in the cathodic direction, however, maximum adsorption (less than before) occurred at about -0.45 volts (SMSE).

In these experiments, time was not allowed for adsorption equilibrium at each potential. (Total time at each potential setting was 5-30 minutes.) The difference in peak heights resulted from differences in surface roughness because of different annealing conditions for the film-electrodes (cf. below).

There existed the possibility that the decrease in maximum peak height and shift of potential at the peak to more negative potentials upon return in the cathodic direction represented the effects of decreasing solution concentration. Such behavior had been noted for platinum by other workers[13,14], using n-decylamine and naphthalene. The behavior for these compounds was interpreted as evidence of electronic interaction between the adsorbed molecules and the platinum. Since n-butane does not contain an electron-rich group as do the others, it was difficult to see why similar behavior should be observed if it results from electronic interaction, assuming that the concentration of n-butane had indeed changed during the experiment. There was also the possibility that the hysteresis resulted from non-equilibrium adsorption. Two additional experiments were run to explore these possibilities further. For these runs the glass-backed, adsorption cell with external counter electrode (Figure 6), in which the rate of n-butane loss was much smaller as shown in Figure 11, was used. One hour was allowed at each potential to

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provide a closer approach to equilibrium adsorption. The solution was not stirred.

In experiment A (cf. Figure 12), the potential was changed step-wise in the anodic direction. In experiment B, a new window-electrode and new solution were used and the potential was changed in the cathodic direction. Potential limits were -0.55 and +0.05 volts (SMSE) in order to avoid the highly reduced or oxidized states of the platinum film. (Hydrogen evolved at -0.7V and oxygen at +0.95V.) Figure 12 shows that the shift in the adsorption peak (about 200 mv) still occurred. A difference in peak height was observed but its significance cannot be assessed because the two platinum films used may have differed in roughness. Total adsorption was much greater in these experiments than in the preliminary experiments (Figure 10). The great increase in amount adsorbed can be attributed to several factors. The electrodes used for the preliminary experiments were platinum-only and had been annealed at 450°C for 45 minutes in the higher adsorbing case and 600°C for 2 hours in the lower adsorbing case (accounting for their mutual differences in that the more severe conditions produced more sintering and therefore a smaller total surface area for adsorption). The electrodes of experiments A and B (and succeeding experiments) were unannealed. Additionally, they contain a porous tantalum underlayment which may accentuate the porosity of the platinum.

Another experiment was run in which time was allowed for adsorption equilibrium (or near equilibrium) at each potential. The solution was not stirred and the first potential setting was at -0.55 volts, as shown by point No. 1 in Figure 13. After equilibrium had been reached, the potential was changed to point No. 2, etc. No shift in the adsorption peak was apparent when the direction of potential change was reversed. Peak adsorption is somewhere between -0.45 and -0.25 volts. It appears that the peak shift in the previous experiments occurred because adsorption equilibrium had not been reached at each potential. Equilibrium required from 2 to 8 or more hours, as shown in Figure 14. Adsorption times of similar length were noted in other work done in this laboratory several years ago[15] where 5 hours were required for the adsorption of a complete compact monolayer of radiostearic acid on vapor-deposited iron films.

Summary

A novel technique for direct measurement of adsorption at metal surfaces, the radiolabeled sorption technique, was successfully adapted for use in studies of the role of adsorption processes in the over-all fuel electrode reaction. Severe mechanical and material problems were overcome and preliminary application to studies of methanol and n-butane in 1N H_2SO_4 at 25°C on platinum electrodes was made.

Methanol adsorbs rapidly to high coverage at open circuit conditions and is easily oxidized by O_2 diffusing to the fuel electrode. Normal butane adsorbs reversibly in the potential range of -0.2 to -0.5V (SMSE). At potentials above and below this range n-butane desorbs. It readsorbs reproducibly within the potential range. Peak adsorption occurs near -0.4V at equilibrium (where coverage may be as high as 0.3). The rates of adsorption and desorption are low--2 to 8 hours being required to reach equilibrium. At shorter times the potential at peak adsorption is shifted to higher or lower potentials depending on the previous treatment of the electrode. The rate of electrochemical oxidation was negligible in the potential range studied (-0.55 to +0.05V, SMSE).

The developed technique is very flexible and broad in scope of potential application. It can be used for study of the effects on fuel adsorption and fuel oxidation of fuel composition, structure and concentration, electrolyte composition and concentration, electrode composition and structure, electrode poisons, electrode potential, and temperature.

INFRARED STUDIES

Studies of heterogeneous catalysis have been greatly benefited in the last few years by application of infrared absorption to solid surfaces.[16],[17] The techniques have been developed to a high degree of utility. Valuable information about bond activation by solid surfaces has been obtained.

Application of infrared to the catalysis at fuel electrodes would be of great benefit. In this portion of the project attempts were made to use special infrared techniques to study adsorption and reaction of fuels at platinum surfaces. Both transmission and multiple internal reflection techniques were considered. Major problems were found to exist with both.

Application of infrared spectroscopy to electrode sorption studies requires:

1) That many monolayers of adsorbate be traversed by the beam. This requires either many reflections from a platinum surface or transmission through a high surface area platinum sample. Sufficient intensity must be preserved in the infrared beam to permit spectral study.

2) That interfering absorption of infrared radiation by aqueous phase

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(or its dissolved fuel) in contract with the adsorbed monolayer be minimized or eliminated.

3) That electronic contact with the platinum be possible.

Transmission Method

Because many traverses of the adsorbed layer must be made to provide a useful infrared signal, transmission studies are best made on a high surface area sample. To provide an adequate surface area, attempts were made to mount a continuous film of platinum on the internal surfaces of a silica aerogel plate.[18] The open spaces of the silica gel would possibly allow flooding with fuel-electrolyte solution and an optical path for the infrared beam.

Calculation showed that for a 400 m^2/g aerogel the platinum content would have to be about 60% for electronic conductivity. Achievement of such high Pt concentrations by impregnation or other methods proved troublesome both for mechanical stability of the aerogel sample and for transparency to infrared.

A silica aerogel sample was ultimately successfully impregnated with 40% Pt but the resulting sample was neither sufficiently infrared transparent nor electronically conducting. Pressing the sample onto a Pt gauze at 15,000 psi did not improve these properties.

Methanol adsorption was studied on silica aerogel alone and on a sample containing about 15% Pt. The Pt sample was poorly transmitting, requiring wide split widths, but allowed some comparisons to be made. Because the absorption of water (H_2O) obscures observation of the C-H and O-H in the fuel, D_2O was used as solvent. Provided exchange of D_2O with adsorbed fuel is slow (which turned out to be the case) observation of the bonds of methanol would be possible since D_2O provides "windows" of weak absorption in the desired regions. On blank silica aerogel, bands similar to those obtained by McDonald[19] were obtained. Figure 15 shows the spectra obtained in the C-H and O-H regions. No significant differences were found for methanol on the Pt-silica sample, but the bands were weak.

Because sufficient transparency and electronic conductivity were found not to be obtainable, no further work was done with transmission methods.

Multiple Internal Reflection Method

An alternative approach, and one which avoids the heavy absorption losses in traversing the solution, is multiple internal reflection. In this technique, an infrared beam, passing through a thin infrared-transparent solid, is made to reflect repeatedly from the inside of the surface. In so doing it passes slightly through the surface, as shown

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schematically in Figure 16. Adsorbed materials near the surface might be scanned by the beam, and, with a large enough number of reflections, a spectrum could be obtained.

Two approaches were examined, one in which coated platinum plates are placed in intimate contact with the IR transparent phase as shown in Figure 16, and the other, where the IR transmitting phase is coated with porous platinum as suggested in Figure 17. The platinum plate method was ruled out by inefficient contacting and excessive loss of radiation. The Pt coating method was studied in more detail.

Existing reflection techniques[20-22] were too insensitive for use although 15-35 reflections were used. Germanium, which had been used previously for such studies[23,24], was selected as IR transparent phase because it is sufficiently transparent in the 1.8-19μ range and is also a semiconductor available with good conductivity so that electrical connection would be easily obtained. Calculation showed that for observing C-H stretch in methanol, 6000 reflections would be needed at monolayer coverage.

Casting of germanium fibers in quartz capillaries was briefly explored but IR transmission was lost by casting. Single crystal Ge plates were used instead. Slices of 40 ohm-cm n-type Ge were lapped or etched from 7 mils to 4-6 mils in thickness to polish them and remove

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imperfections. The edges were beveled at 45° (for maximum number of reflections). The final dimensions were 32 x 25 x ~0.15 mm, which allowed about 200 reflections.

Three paraffin-coated, polished, Ge plates were mounted in the entrance optics of a Perkin-Elmer Model 112 Spectrometer. The intensity of the paraffin bands obtained, compared with paraffin transmission spectra, revealed that the effective penetration of the internally re-flected IR into the external (paraffin) phase was less than 1000 Å. The paraffin was cleaned from the Ge surface with boiling CCl_4 resulting in disappearance of the C-H bands.

A coating of stearic acid was applied to the same samples by dipping them into molten stearic acid, rinsing in benzene and drying. An absorption spectrum, Curve a of Figure 18, was obtained. Both car-bonyl and C-H stretching bands were seen. Repeated washing in boiling benzene did not remove (Curve b) all of the melt-applied stearic acid seen in Curve a. A known monolayer was applied to both sides of each plate by the Langmuir-Blodgett film-balance technique. The resulting bands (Curve c) were not as intense as those in Curve a showing that the beam penetrates farther than one monolayer into the phase adjacent to the germanium. The C-H bands of Curve c show an intensity of about 0.1 absorbance unit, approximately the value expected for 200 reflections.

Subsequent tests using a Perkin-Elmer 12C Spectrometer, showed that C-H stretch was observable on a single germanium wafer immersed in D_2O (proving that this technique was workable), and that tetradecanol was observable through a 100 Å coating of platinum oxide on quartz (suggesting that use of Pt on Ge might work). A cell was designed for use with liquid phase in contact with multiple Ge wafers as shown in Figure 19. (The wafers are easily cracked in assembling this cell, however.)

The major problem to this point was the limited efficiency of transmission of IR through the plates. Optical polishing to less than 4 mils, positioning the sample in the exit rather than entrance optics, and use of a highly-sensitive, new Bechman IR-9 Spectrometer did not sufficiently improve the transmission.

It was subsequently proved that major losses during transmission occur in transit through the germanium phase. When a wafer was cut in half and rebeveled, the transmission increased five-fold. Losses no doubt occurred at imperfections in the crystal but improving the already-tedious polishing technique did not lead to corresponding improvements in transmission.

Using the best techniques and the Beckman IR-9, two Ge wafers, first uncoated and then coated, respectively, with 50 Å and 200 Å of

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sputtered platinum revealed major IR losses in the coated samples. Transmission through the 50 Å-Pt sample decreased to 30-40% of the uncoated value, while the 200 Å-Pt sample was virtually opaque. This result revealed a severe limitation in the application to fuel electrode studies.

It was also found that the Ge wafers retained organic contaminant after use, which could not be removed completely.

Summary

At this point sufficient information had been gained about the techniques tried to rule them out for general application to the fuel electrode. Multiple internal reflection with coated germanium wafers and 200 reflections can give marginally useful spectra and, where a given answer warranted the exceptionally tedious procedure, might give insight on a particular problem. But the limitations imposed by limited reflections, non-reusability of samples and absorbance of metal coatings do not allow its use for exploratory purposes. For these reasons, no further work was done in the infrared area.

ELECTRON-SPIN-RESONANCE STUDIES

The electron-spin-resonance portion of the project had as its objective the search for and study of free-radical intermediates in fuel electrode reactions. Using highly refined equipment, peaked to maximum sensitivity, no signals for common fuels were observed although electro-generated radicals from relatively complex organic molecules in aqueous solution were easily observed. Using complex molecules as pilots, exploration of conditions and additives revealed important effects which, however, did not lead to observable spectra for common fuels. Work was halted when reasonable prospects were exhausted. The possibility that free-radical intermediates are indeed generated but are electrode-bound in a way that they cannot be observed by electron-spin-resonance was not ruled out by this work. The approach and results are summarized below.

Approach

One of the two prominent mechanisms for hydrocarbon electro-chemical oxidation is called the radical-ion mechanism.[25,26] This presumes free-radical intermediates in the reaction. At present, the most promising method for studying small quantities of free radicals is electron-spin-resonance spectroscopy. The spin of an unpaired electron in the presence of an external magnetic field may become oriented in two ways, either against or with the field. These two orientations have

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slightly different energies and if radiation is supplied, a transition from one orientation to the other may occur. The energy difference between two possible spin orientations is proportional to the strength of the applied magnetic field. To bring about this type of transition, radiation in the microwave region (10^{10} cycles/second) must be used. The wave length of the incident radiation is kept constant while the intensity of the magnetic field that surrounds the sample is continuously varied. Small changes in the adsorption of microwave energy by the sample are detected. Radical concentrations as low as 10^{-8} molar have been observed. Also, the mean lifetimes of radicals can be estimated.

The observed adsorption bands frequently have fine structure; that is they are composed of two or more thin bands lying close together. This splitting results from interactions between the spin of the unpaired electron and the spins of one or more nuclei. By analysis of the fine structure it is often possible to learn whether the unpaired electron is localized on a single atom or spread over a number of atoms. Thus, it is sometimes possible to uniquely define the presence of, amount of, and composition of free-radical intermediates.

Until recently, it was thought that application of electron spin resonance to electrode processes was impossible because of the high

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dielectric constant of aqueous solutions. Recent workers have shown that such an application can be made.[27,28] Entire half cells have been placed inside the resonance cavity of ESR equipment and unpaired electron intermediates established. Our work attempted application to the fuel electrode.

Technique

For these studies a Varian Associates Model V4500 electron-spin-resonance spectrometer was used, operating at x-band frequencies of about 9500/second. For increased sensitivity a Varian Model V4560 100 KC Modulating Unit was purchased and used. Wave guides of the RG52 type and flanges of the VG39 type were employed. A Microwave Associates Model MA423 A diode detector and an improved V-153C Klyston tube were used in the circuitry. Considerable development work was done on the designs of the cavity, coil, and cell to achieve maximum sensitivity.

The final designs of the cavity, coil and cell are shown in the photograph of Figure 20. The cavity was machined from nylon and lined with a thin coating of silver paint (General Cement Co.). A cross-sectional view of the pyrex cell is shown in Figure 21. This cell design had only one electrode within the cavity because it was found that free-radical generating reactions sometimes occur at both electrodes leading to confused spectra. The platinum electrode was flattened and oriented

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plane parallel to the tuneable end of the cavity. The cell design is similar to the Varian V-4546 sample cell and to one described in the literature.[28]

Preliminary Results

In preliminary work it was determined that no ESR signals occur in the region of interest for platinum, graphite or the cavity and cell materials. Radicals chemically generated from t-butyl peroxide in acetic acid and 1,1 diphenyl-2-picryl hydrazyl in benzene (DPPH), and electrochemically generated from p-phenylene diamine (PPD) in aqueous buffers (pH4-5) and p-aminophenol (PAP) in aqueous acetic acid at slightly alkaline pH gave clear ESR signals. DPPH radicals could be observed at the 10^{-6} M concentration level with the highly sensitive system. Increasing the specific surface area of platinum by platinizing or using platinized carbon did not enhance the signal obtained with PPD showing that the species yielding the ESR signal was probably in solution rather than affixed to the electrode surface. Substitution of D_2O for H_2O in generating radicals from PPD gave enhanced gross signal intensity at expense of hyperfine resolution. Adjustment of pH to 4-5 for PPD or to ~9 for PAP gave maximum signal strength.

Application of the apparent benefits of pH control and D_2O substitution to alcohol fuels such as methanol, ethanol and t-butanol did not lead to resolvable ESR signals.

Attempts to Improve Radical Stability

Electrochemical oxidation of many organic materials is thought to involve free-radical intermediates, but in preliminary work, anodically generated free radicals were detected only in cases where the organic molecule contained a stabilizing aromatic pi electron system. Radicals from electrooxidation of aliphatic materials were not detected.

Possible reasons for the inability to detect radicals are as follows:

1. Free radicals might not be formed.

2. Free radicals formed might have such short lifetimes that a steady state concentration large enough for detection cannot be achieved.

3. Free radicals formed might interact with the electrode surface in a manner which prevents their detection or accelerates their disappearance.

4. Free radicals formed might interact with some molecule in the solution in a manner which prevents their detection or accelerates their disappearance.

The kinds of information about free radicals given by an ESR spectrometer can be classified in the following manner:

1. The intensity of the recorded spectrum.

2. The "g" value of the resonance.

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3. The line shape of the resonance peaks.

4. The hyperfine structure.

5. The stability of the paramagnetic centers (spin centers) observed.

If an electron-spin-resonance signal of a free radical is observed the recorded spectrum will give information on all of these. However, if stability, 5, is too low, no signal and no information is obtained.

The failure to detect radicals during alcohol oxidation might result from poor stability of generated radicals. Several approaches could be taken to increase the stability of the free-radical inter-mediates.

1. Elimination of molecular oxygen from the solutions. Oxygen accelerates the decay of radicals.

2. Putting soluble additives into the solutions. Additives might slow the decay of radicals or upset interactions of radicals with electrode or solution species. Basic additives in a certain pH range enhance signals from radicals generated from para-amino phenol.

3. Freezing the solutions. Freezing might delay the disappearance of radicals.

4. Low temperature generation. Low temperatures may retard disappearance of radicals allowing current controlled generation to build a high enough steady state concentration of radicals.

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5. Increasing viscosity of the solution. If radicals decay by combination or wall reactions, higher viscosity might retard their disappearance.

6. Providing a solid surface for adsorption of radicals generated and freed into the solution. Steady state concentration might be increased by adsorbing radicals cn a suspended high surface area solid or a gel. Strong adsorption might immobilize radicals and prevent their disappearance by combination.

Each of these possible stabilizing factors was explored using p-aminophenol (PAP) as a pilot reactant. Positive effects with PAP were found for O_2 elimination and addition of soluble additives (pH control). No beneficial effects were found for the other approaches, but they were not exhaustively explored.

Elimination of oxygen, which accelerates the rate of decay of radicals, was found beneficial in observing electrogenerated radicals from PAP. Oxygen was removed from the samples by scrubbing the solutions with oxygen-free nitrogen. In Figure 22a is shown the spectrum obtained for radicals being electrogenerated from PAP at pH 9.5 in O_2-free solution. Inspection of the ESR spectrum indicated that the site of oxidation was the amine nitrogen. At point X in Figure 22b is seen a rapid decrease in signal intensity resulting from earlier injection of oxygen. Elimina-

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tion of oxygen from solutions of alcohol fuels did not yield observable ESR signals.

In studies of soluble additives a correlation of ESR signal intensity for PAP with pH was found. Maximum intensity was found at about pH 9.6 (cf. Figure 23). Borate, carbonate and cyanide ions appeared to enhance the signal while potassium ion seemed to suppress it. Earlier it had been found that signals from radicals generated from p-phenylene diamine were maximum at pH4-5. When pH, cyanide ion and carbonate ion were tried with alcohol fuels such as methanol, ethanol, t-butanol, benzyl-alcohol and p-nitrobenzylalcohol (the latter two to seek stabilization through the pi electron system of the ring), no ESR signals were obtained.

Provision of a high surface area solid in the electrolyte in hopes of trapping possible generated radicals was unsuccessful with both PAP and several alcohols. Acidified sodium meta-silicate, Cabosil HS-5 silica gel and powdered magnesium hydroxide were tried.

Freezing the solution was found to stop generation of radicals and eliminate the ESR signal. Cooling the solution did not remove the signal but did not enhance it. Changes of viscosity near the freezing point of aqueous solutions or in alcoholic solvents at room temperature did not prove beneficial.

Summary

    During the entire course of the experimental search for free-radical intermediates from anodic oxidation of aliphatic fuels, no ESR signals attributable to these fuels were found. Using a relatively more stable, anodically generable, radical (that from p-amino phenol) as a pilot, several potential radical-stabilizing factors were explored. Among the factors studied, pH, elimination of oxygen, and the presence of certain additive salts were identified as having a positive effect on the observability or intensity of ESR signals. Application of these factors to systems containing aliphatic fuels did not lead to observable ESR signals for such fuels. No further work was carried out in this area.

    The results of this work did not rule out the possibility that radical intermediates are generated from aliphatic fuels but are too unstable or are associated with the electrode in such a way that they cannot be detected by ESR.

DOUBLE PULSE STUDIES

This portion of the project had as its objective the characterization of activation polarization for fuel electrode reactions using the double pulse method of Gerischer and Krause.[29] Problems with excessive electronic noise and poor amplification were encounted early in the work and, in view of probable sluggishness in the adsorption and oxidation processes, coupled with the need for measurements in the microsecond time scale, further work was halted early in the project. Preliminary work with mercurous and cadmium ions was reported in the first five quarterly reports.

DIFFERENTIAL CAPACITANCE STUDIES

Differential capacitance measurements were employed to study the extent and type of adsorption of fuels, intermediates and products of fuel electro-oxidation and other solution species as a function of electrode potential with the object of learning more about the role of sorption processes occurring during oxidation at electrodes. Detailed information was obtained about the adsorption kinetics of methanol in 1M H_2SO_4 at 25°C as a function of concentration and potential. Some results for formic acid and propylene were also obtained. Suitable conditions were not found for capacitance studies of light hydrocarbon fuels.

Approach

This approach was chosen on the basis that neutral organic molecules, adsorbed at the electrode-solution interface often cause a lowering of the electrode capacitance because of the change in dielectric properties at the electrode-solution interface when water molecules are replaced by organic molecules. An important advantage of this approach over coulometric methods is that adsorption can be followed over a time interval without disturbing conditions at the electrode to a significant extent.

Apparatus

Apparatus for differential capacitance measurements employing

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a modified square wave charging technique was constructed. Figure 24

shows a block diagram of the measuring system. Figure 25 is a diagram

of the cell. Test electrodes were bright platinum wires of 0.025"

diameter sealed in soft glass. A detailed description of equipment and

experimental procedures is available in the Fifth Quarterly Report[30]

along with a discussion of the theory behind the method.

Results

Experimental work commenced using methanol as adsorbate.

Figure 26 shows curves of capacitance versus electrode potential for

bright platinum at constant potential under steady state conditions. The

solutions were 1M H_2SO_4 at 25°C containing various amounts of methanol.

Potentials were measured using a $Hg/Hg_2SO_4/2N$ $H_2SO_4 + Hg_2SO_4$ (Sat'd) elec-

trode and all potentials mentioned refer to this electrode. The lowering

of the capacitance with increasing methanol concentration agrees with

theory and indicates increasing adsorption of methanol. The potential

region in which the capacitance lowering occurs and the hysteresis

behavior shown by the dashed curves coincide with available data on the

platinum surface oxidation regions and leads to the view that adsorp-

tion of methanol occurs only on an oxide-free surface. In order to com-

pute surface coverages from the data, use was made of Frumkin's relation:

$$C = C_{\theta=0}(1-\theta) + C_{\theta=1}\theta$$

where the C's correspond to measured capacities for coverages θ, 0 and 1 and θ is the methanol surface coverage. On this basis θ values were computed for potentials between 0.0 volts and -0.2 volts. In this region θ is nearly independent of potential. Figure 27 is a plot of θ values thus obtained versus log methanol concentration. This result suggests Temkin isotherm behavior.

Adsorption kinetics were explored in the next step. To obtain reproducibility, it was necessary to program the potential. Oxygen was evolved at the test electrode briefly, followed by treatment at 0.2 volts to remove dissolved oxygen from solution. The potential was then switched to a value in the range 0.0 to -0.2 volts and adsorption of methanol versus time was followed. Figure 28 is a plot of θ versus log adsorption time. The points are an average of data taken at 0.0, -0.1 and -0.2 volts. Adsorption rates appeared to be independent of potential over this range. The nearly linear behavior of the plots indicates Elovitch rate behavior. Although the intercepts of the curves vary as log methanol concentration, this is not sufficient to deduce a reaction order with respect to methanol concentration. An attempt was made to fit the data to a relation of the type:

$$d\theta/dt = kC_{MeOH}^{p}(1-\theta)^{q}\exp\left[-\Delta H_{o,ads}^{*}(1 + \alpha\theta)/RT\right]$$

to which more physical significance can be attached. Figure 29 shows,

along with the rate data, computer results for the equation in the form:

$$d\theta/dt = K_1 C^p (1-\theta)^q e^{-K_2\theta/RT}$$

with $T = 298°K$, $p = 1$, and $q = 2$, for a particular set of K's. Although these are not unique solutions, they are one of the best fits for the data. Data at several temperatures would be useful. Some attempts in this direction were made, but a 15° rise in temperature failed to show temperature dependence. Apparently a broad range of temperatures is required.

Rates of adsorption of formic acid were measured over a range of potentials. A solution 5.7×10^{-3} molar in formic acid and 1 molar in sulfuric acid at $25°C \pm 1°C$ was used. Figure 30 shows the coverage versus time curves obtained at potentials in the range -0.5 to 0.0 volts. Contrary to behavior seen with methanol, the data are potential dependent. An apparent saturation value of $\theta = 0.85$ is reached in 10-20 minutes in the range -0.5 to -0.3 volts but hours are required at more positive potentials. It was found that adsorption rates increase with formic acid concentration. Figure 31 shows θ versus log adsorption-time curves for some of the plots of Figure 30. Two nearly linear regions can be seen, contrary to the behavior of methanol, where single stage Elovitch behavior was noted.

Formic acid demonstrates more complex adsorption behavior than

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methanol. A stronger adsorption is indicated for formic acid since higher saturation coverages are reached at comparable concentrations. Rates of adsorption are similar in the range -0.3 to -0.5 volts. At more positive potentials, formic acid adsorbs at a slower rate.

The slow approach to saturation coverage at potentials noble to -0.3 volts might be associated with byproducts of anodic current flow. At potentials positive to -0.3 volts prolonged anodic current flow occurs. To explore this further an experiment was performed as follows. After an electrode attained saturation coverage at either -0.5, -0.4, or -0.3 volts, the potential was abruptly changed to some value in the range -0.2 to 0.0 volts. The resultant anodic currents rose slowly to some value and then dropped off with time. During the current increase the coverage decreased to some value and remained constant thereafter. When the potential was then returned to the range of rapid adsorption (-0.5 to -0.3 volts), the coverage failed to increase to saturation values even after hours. These results suggest partial but irreversible cover-age by an intermediate of formic acid oxidation whose effective di-electric constant in the adsorbed state is higher than for adsorbed formic acid. Elovitch behavior and the occurrence of breaks in the rate curves suggest that two kinetic stages are involved in the adsorp-tion process. This behavior could also be caused by buildup of inter-

mediates of electro-oxidation on the surface. It is interesting that the break in the -0.5 volt curve in Figure 31 is decidedly less distinct than for the others.

A variety of hydrocarbons was surveyed for adsorption activity. Ethane, propane, butane, ethylene and t-2-butene showed no activity for adsorption on bright platinum in 1M H_2SO_4 at temperatures up to 80°C after several hours of exposure. An activation technique employing potential programming similar to the case of methanol and formic acid was tried. The lack of activity could possibly be explained by the very low solubility of these gases in aqueous solutions and the consequent low equilibrium surface coverages.

In the case of propylene some success was had. Figure 32 shows differential capacitance versus electrode potential curves for a solution saturated with propylene in one case, and with a 50% mixture of propylene and helium in the other. A capacity minimum occurs at 0.0 volts as for methanol and formic acid solutions. A general capacity lowering occurs with increasing propylene concentration. Adsorption appears to occur over a much broader potential range than is observed for methanol or formic acid. In the potential range negative to 0.0 volts the observed hysteresis in the plots suggests irreversible desorption of propylene at sufficiently negative potentials.

A solution of 85% H_3PO_4 at 140°C was used to test for adsorption activity by hydrocarbons at temperatures higher than could conveniently be obtained using sulfuric acid solutions. Figure 33 shows the results of capacitance measurements without fuel in this electrolyte. Along with this is the data for runs made with a propane saturated solution. The adsorbate saturated curve shows a capacity decline beyond that seen for the adsorbate-free solution in the regions 0.0 to 0.3 volts and 0.2 to 0.5 volts depending on the direction of potential change. Adsorption appears to occur in a restricted potential range positive to that where oxidation would be expected. The sharp decline at 0.3 volts, and the hysteresis behavior between 0.3 and 0.6 volts for the adsorbate-free curve, appear to be associated with formation and removal of surface oxide. Examination of the adsorbate-saturated curve suggests that propane is adsorbed on an oxide free surface.

Summary

The results of fuel adsorption studies employing the differential capacitance method led to a number of conclusions which can be summarized as follows:

1. Both methanol and formic acid are strongly chemisorbed on oxide-free platinum electrodes in sulfuric acid solution. Methanol adsorption follows Temkin isotherm behavior.

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2. Rate of adsorption studies indicate activated adsorption of both fuels with Elovitch rate behavior. Diffusion appears not to affect rates under the conditions of the experiments performed. Formic acid shows more complex behavior than methanol, and adsorption may be influenced by byproducts of anodic current flow.

3. Adsorption of hydrocarbons proved difficult to detect, possibly because of their low solubility in aqueous solutions, but possibly also due to a more difficult path for adsorption at moderate temperatures, in comparison with polar oxygenated compounds. Positive results were obtained for propylene in 1M H_2SO_4 at 80°C and propane in 85% H_3PO_4 at 140°C.

4. Electrode pretreatment and potential programming are necessary to promote activation of the platinum surface for adsorption and in order to achieve a useful degree of reproducibility.

FUEL ELECTRO-OXIDATION STUDIES

The X-Y pulsed polarization and chronopotentiometric techniques originally planned for the project are really methods of studying electro-oxidation at the fuel electrode. Other related methods which were applied to electro-oxidation studies were potential step and potential sweep techniques. These are all combined in this final report under this section. The studies did not lead to successful application of the X-Y technique to studies of hydrocarbon reactions, mainly because of sluggish relaxation of polarizations. Some results were obtained for paraffins, olefins, methanol and formic acid by potential step and potential sweep methods.

Initial observations of the systems studied in the sorption studies revealed that electro-oxidation of methanol, formic acid, and selected hydrocarbon was severely polarized at bright platinum electrodes in 1M H_2SO_4 at room temperature. In searching for means to "activate" the electrode for these processes, it became apparent that non-steady state conditions would be the rule, but with appropriate electrode pretreatment and potential programming a moderate degree of reaction could be induced and a practical degree of reproducibility of the polarization behavior could be attained. Two methods were employed in studying polarization behavior which are appropriate for the conditions imposed

by the systems studied. These are the voltage step method and potential sweep voltammetry. Both approaches were to provide information which could be used to program these systems for the X-Y pulsed polarization approach.

Voltage Step Method

Controlled potential current-time data was obtained for methanol and formic acid in 1M H_2SO_4 at $25 \pm 1°C$. The potential step is accomplished by use of a mercury relay to switch from one reference potential source to another. Figure 34 shows a block diagram of the electronic setup. A description is available in the Ninth Quarterly Report.[31] Figure 35 shows the current-time curve obtained at -0.2 volts for methanol oxidation after the following activation procedure:

1. 1.2 volts (O_2 evolution) for 1 minute.

2. 0.2 volts with helium flushing to remove dissolved O_2 for 5 min.

3. Potential then switched, using the relay, to a value in the fuel electro-oxidation region, 0.0 volts to -0.2 volts, and the solution unstirred.

This program was used also for the sorption studies. The solution was 0.0424M in methanol. The potential in step 3 was -0.2 volts. The initial portion of the trace after switching cannot be seen because of large cathodic film-reduction currents. The current then becomes anodic with a

maximum followed by a slow decline. This suggests that methanol oxidation occurs most rapidly on a freshly reduced surface.

A linearized presentation of the anodic current versus time data is presented in Figures 36, 37 and 38 for the three potentials and over a range of methanol concentration. The best fit is obtained with an i versus $1/t^{1/2}$ relationship. The slopes $\Delta i/\Delta t^{1/2}$ are plotted versus methanol concentration as a log-log plot in Figure 39. The slopes of the log-log plots, $\Delta \log (\Delta i/\Delta t^{-1/2})/\Delta \log$ conc. MeOH are noted in the Figure. The anodic current-time curves revealed a rapid current decrease to zero current for the -0.2 and -0.1 volts cases. At 0.0 volts, the anodic currents declined very slowly if the solution was unstirred. Stirring caused a much more rapid current decline at all three potentials. The maximum anodic currents ($i_{max.}$) are plotted in Figure 40 as a function of methanol concentration. Three or four pretreatment cycles were usually needed to achieve a constant value of $i_{max.}$, which increased to a steady value with repeated cycles.

The results show that methanol oxidation can occur at relatively high rates at potentials as negative as -0.2 volts provided the electrode has been previously oxidized. Anodic currents drop off very rapidly with time at potentials negative to 0.0 volts. The linearity of the i versus $t^{-1/2}$ curves could be explained if the reaction were diffusion controlled

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and reversible or diffusion controlled with the heterogeneous rate constant: $k > D^{1/2}/t^{1/2}$. In either case the current, i, is given by

$$i = nFAD^{1/2}C_{MeOH} \cdot 10^3/\pi^{1/2}t^{1/2} \cong 1.7 \times 10^5 \, C_{MeOH}/t^{1/2}$$

assuming semi-infinite linear diffusion[32] where n = number of electrons transferred, $F = 10^5$ coulombs/eq., C_{MeOH} = concentration of methanol in moles/l; D = diffusion coefficient of methanol $\approx 10^{-6}$ cm^2/sec. and t = time in seconds. A slope of $1.7 \times 10^5 \, C_{MeOH}$ is predicted taking n as 6. Anodic currents observed are thus several orders of magnitude lower than predicted by this relation. In addition, the slopes of the i versus $t^{-1/2}$ plots are not linear in C_{MeOH} as can be seen from an inspection of Figure 39. The concentration dependence of i_{max}. predicting first order kinetics at zero time of polarization seems reasonable, though. Only small deviations from semi-infinite linear diffusion were expected (the electrode diameter was roughly one millimeter and the volume of solution about one-half liter). In addition, convection was probably unimportant over the short time (less than 20 seconds) involved in these studies. At first sight one might conclude that diffusion of methanol to the electrode is not rate limiting under the conditions of these experiments. One might consider a pre-electrochemical step which produces the electroactive species which then diffuses to the electrode,

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however, from the concentration dependences observed for the slopes of the
i versus $t^{-1/2}$ curves, the magnitude of the currents involved, and the
very small degree of dissociation of methanol in aqueous acid solutions
such a step seems improbable.

The possible role of the state of the platinum surface during
the anodic current decay should also be considered. A change in the
state of the surface could be caused by reduction of the platinum surface
oxide, producing a heterogeneous surface containing a distribution of
active sites, which decay with time. Or, the state of the surface could
be changed by partial reduction of platinum surface oxide to a semi-
reduced form which is catalytic for electro-oxidation of methanol and
which decomposes with time.[33] In either case the process should follow
the observed kinetics for methanol oxidation. The observed methanol con-
centration dependences may be caused by an involvement of methanol in one
of these processes. An additional explanation for the observed behavior
could be that only a small portion of the available platinum surface is
active for oxidation and that current densities at these sites could be
sufficiently high to lead to apparent diffusion controlled behavior.

Figure 41 shows anodic current versus time for a solution 0.0057
molar in formic acid using the same potential program as that used for
methanol. Anodic currents are seen at potentials of -0.3 volts. Apparently,

a lesser degree of polarization is observed with formic acid than with methanol. The form of the current versus time curve is quite similar to that seen for methanol. At -0.2 and -0.1 volts formic acid comes closer to achieving steady state oxidation currents than methanol.

Similar studies were conducted of a solution of 1M H_2SO_4 at 80°C saturated with ethylene. Figure 42 shows the results of these studies. Currents increase with potential between -0.3 and +0.1 volts. No anodic current flow occurs during the +0.3 volt run. This was expected because the surface oxide is probably still intact at this potential. In repeated trials, the 0.2 volt runs (not shown in Figure 42) were either like the 0.3 volt run or the anodic currents underwent a slow increase with time. These differences probably reflect differences in the relative contribution of surface oxide reduction to the net current. For the runs at -0.3 to +0.1 a rapid current decay was observed at short times (several seconds). At longer times (30 seconds and greater) the system approaches steady state conditions. The currents obtained at the several controlled potentials exhibit Tafel behavior. Table II lists the Tafel slopes obtained from the data of Figure 42. At times less than six seconds the slope was 0.29. At times longer than 30 seconds the slope was 0.22. A shift in the slope occurs between six and thirty seconds. The slopes are based on only four or five points in each case.

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It should be noted that the occurrence of Tafel behavior indi-
cates activation control possibly superimposed on any relatively stable
partial diffusion control that might also be present.

TABLE II

TAFEL SLOPES FROM CONSTANT-POTENTIAL CURRENT-TIME DATA
OF FIGURE 42 FOR ETHYLENE ON BRIGHT PLATINUM AT 80°C

Time after Start of Polarization, Seconds	Tafel Slope	Range of Linearity, Volts
1.5	0.29	-0.3 to +0.1
6	0.29	-0.3 to +0.1
6 to 30	decreases	-0.2 to +0.1
30	0.22	-0.2 to +0.1
49	0.22	-0.2 to +0.1

The shift in Tafel slope shown in Table II suggests that the
mechanism changes with time during polarization after exposure of a
freshly reduced platinum surface. The Tafel plots also showed a continu-
ous shift in the intercept as a function of time. This may be indicative
of a continually decreasing area effective for oxidation. The behavior
observed for ethylene with respect to potential region of oxidation and
to polarization-time behavior is very much similar to that for methanol
and formic acid. This suggests that some condition of the platinum sur-

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face might determine the electrochemical parameters of fuel oxidation to a greater extent than the specific properties of a particular fuel.

Potential Sweep Voltammetry

Potential sweep studies of several hydrocarbons were made using a Brinkmann Model 61-R Fast Rise Potentiostat and a conventional, mechanically driven sweep, reference-voltage source. A description of the experimental details is available in the Seventh Quarterly Report.[34]

Figures 43 and 44 show potential sweep scans for several hydrocarbons and a blank (helium through cell). The scan rate was 17 mv/sec. and the temperature was 80°C. The electrode potential was swept from -0.2 volts to 1.1 volts and back until reproducible peak heights could be obtained. The scans seen in Figures 43 and 44 represent steady state conditions with respect to peak heights. Peaks 3 and 4 correspond to oxygen evolution and surface oxide reduction, respectively. Peak 1 represents fuel oxidation as it occurs on the cathodic sweep. The close proximity of peaks 1 and 4 may result in mutual suppression of peak heights. It seems probable that the anodic current flow occurring during peak 1 represents the net current or the difference between fuel oxidation current and surface-oxide reduction current. Some chemical reduction of the surface oxide probably occurs also, and this process also contributes to the suppression of the surface oxide reduction peak. It is possible

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that peak 1 represents only a portion of the true fuel oxidation current.
Peak 2 occurs on the anodic sweep and over a broader potential range
than peak 1. In this case, reaction occurs mainly at the onset of the
region of surface oxide formation. Judging from the relative magnitudes
(anodic versus cathodic direction of the sweep) of the fuel oxidation cur-
rents at potentials less positive than +0.2 volts, it would appear that
the reaction is less impeded at a freshly reduced surface (peak 1) than
on one recently subject to fuel oxidation (onset of peak 2).

The anodic peak heights in Figures 43 and 44 increase in the
order: propane $<$ trans-2 butene $<$ 2-butene (mixed cis and trans) $<$ 1-
butene $<$ propylene $<$ ethylene. From this it can be tentatively concluded
that olefins oxidize easier than alkanes. In addition, the least hindered
olefins appear to oxidize most rapidly. This could be due to greater ease
of chemisorption, or to the enhanced solubility of the smaller olefins.

To determine if transport of fuel to the electrode plays a role,
the effect of solution stirring was noted. If the flow of gaseous olefin
was stopped in the case of any of the olefins studied, a sharp drop in
the peak height was observed on the following sweep. If helium flushing
was then started the lowered peaks dropped slowly with time during helium
flushing. These results suggest that transport, in addition to other
slow processes, is involved in the overall oxidation mechanism. Figure 45

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shows potential sweep scans for ethane and a blank (helium through cell), taken under the same conditions. The scans illustrated in Figure 45 show steady state peak height. The difference curve shown in the inset of Figure 45 shows a low peak at about +0.05 volts. The scans shown are those for a sweep rate of 17 mv/sec. Runs were also made at 8 and 5 mv/sec. The peak current remained relatively constant at about 25 microamps. The potential at the peak current remained at +0.05 volts. The constant peak current suggests diffusion control. The peak potential of +0.05 volts contrasts with the peak potential of +0.3 volts common to the scans with various olefins.

The ethane results at 17 mv/sec. are compared with results for ethylene and propane at the same conditions in Figure 46. Larger currents are obtained with ethane than propane.

When the electrode is anodically pretreated at 1.2 volts and swept in the cathodic direction starting at 1.1 volt, the anodic fuel oxidation peak is partially obscured by the cathodic oxide reduction peak. A cathodic pretreatment was established in which the electrode is held at -0.6 volts and is subsequently not made more anodic than +0.5 volts. This pretreatment was designed to eliminate, or restrict to low levels, the amount of surface oxide generated and thereby the amount of cathodic reduction current during the sweep. Comparisons of oxidation-peak poten-

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tials of the anodic-going and cathodic-going sweeps could then be made.
Figures 47 and 48 show the results in the two cases.

Figure 49 shows mixed surface oxide reduction and fuel oxidation peaks. The currents are higher and more anodic on the "reduced" electrode. However, the actual fuel oxidation currents may be higher for the "oxidized" electrode but hidden by the reduction peak. Comparison of the paraffin curves with the helium curves shows current-peak potentials of about +0.05 for both anodic and cathodic sweeps. The current-peak potentials for the olefins appear more anodic in the cathodic-going sweeps, particularly for the "reduced" electrode where the oxide film reduction current is small.

The fact that no outstanding difference in peak current was observed for paraffins between "oxidized" and "reduced" platinum electrodes does not necessarily mean that the rates are kinetically the same. The low concentration of fuel at the electrode may be controlling the current and masking a possible difference in rate. The 0.25 volt difference in peak potential between paraffins and olefins may be real.

X-Y Pulsed Polarization Method

The X-Y pulsed polarization method is capable of yielding current voltage behavior at short times--hence at low net passage of current in the faradaic process. It was expected that this method would be useful

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where slow adsorption of fuel prevented obta'ning I-V data because fuel was depleted in the I-V measurement. This expectation was not realized mainly because relaxation of polarization was too slow, requiring such long pulse lengths that other methods could be used.

The apparatus setup, which was similar to one reported in the literature[35], is shown in block diagram in Figure 50. Descriptions of technique are given in earlier reports.[30,36]

The method, applied to hydrogen, gave a reasonable check of published results.[35] Studies of activation of platinum for ethylene in 1M H_2SO_4 at 80°C, discussed above, under Potential Step Method, showed a time dependence of current versus time after activation at O_2 evolution (cf. Figure 42). At times of the order of 10-20 seconds after activation, the current reaches a relatively steady value at controlled potential. X-Y studies made at this "steady state" showed too small a potential swing suggesting that the relaxation of polarization was too slow for X-Y studies to be useful. Currents with small paraffins were too small for study. It was concluded that this method would not be generally useful for fuel electrode studies.

Chronopotentiometry

The method of Anson[37] was planned to be applied to fuel electrode studies. Here fuel would be adsorbed under favorable conditions

(e.g., gas phase), the electrode would be immersed in electrolyte, and the amount adsorbed determined by chronopotentiometry. Because 1) pretreatment of the electrode is important in activating the electrode for adsorption and oxidation, 2) the sites active for gas adsorption may not be the same ones active in solution, and 3) the rates of oxidation (i.e., currents) obtainable were too small, this method was not applied.

Summary

The conclusions reached from kinetic studies of the electrooxidation of several fuels employing the voltage step method and potential sweep voltammetry are outlined below:

1. Methanol, formic acid and ethylene are most readily oxidized on a freshly reduced platinum surface. At a fixed potential anodic currents decay with time suggesting either slow removal of active sites or buildup of intermediates on the electrode surface. Polarization appears to decrease in the order saturated hydrocarbon $>$ unsaturated hydrocarbon $>$ methanol $>$ formic acid.

2. The current decay with methanol follows an i versus $t^{-1/2}$ relation, but anodic currents were too high for diffusion control at the methanol concentrations employed. In addition, stirring had the effect of increasing polarization. A small, but active, fraction of the surface supporting anodic oxidation at high current densities could account for this behavior.

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3. Maximum currents varied linearly with methanol concentration indicating first-order dependence at zero time of polarization.

4. Potential sweep voltammetry showed anodic peaks for fuel oxidation to occur at potentials at which little or no surface oxide was present on the electrode. Peak heights increased in the order propane $<$ ethane $<$ t-2 butene $<$ 2-butene $<$ 1-butene $<$ propylene $<$ ethylene. Apparently the less hindered hydrocarbon reacts at the highest rates. Mass transport appears to play a role in the overall kinetics.

The X-Y pulsed polarization method was found to be not generally useful because of the slow relaxation of polarization and too-small oxidation currents.

Chronopotentiometry of pre-sorbed fuels was not applied because of the discovered need of activating the electrode by electrochemical treatments and because of too-small oxidation currents.

IRRADIATION OF ELECTRODES

To test the effect of radiation on the activity of fuel electrode catalysts, plans were made for limited studies of a variety of electrocatalysts alone and supported on carbon. The X-Y pulsed polarization technique was to be used to rapidly measure current-voltage characteristics in the presence and absence of reactor irradiation. Because the X-Y technique was found not to be useful, this work was not completed.

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FIGURE 1

DIRECT MEASUREMENT OF ADSORPTION
OF RADIO LABELED FUEL

COUNTER
ELECTRODE

SOLUTION CONTAINING
C^{14}-LABELED FUEL

METAL FILM

ELECTRICAL
CONTACT

SUBSTRATE

BETA RADIATION

PROPORTIONAL COUNTER TUBE

FIGURE 2

THICKNESS AND PENETRABILITY OF SPUTTERED
PLATINUM FILMS

FIGURE 3

MICA WINDOW MOUNTING

FIGURE 4

ADSORPTION CELL WITH INTERNAL COUNTER ELECTRODE

TUBE SEALED IN WITH EPOXY RESIN

0.5mm PYREX CAPILLARY TUBE

RING-WINDOW ASSEMBLY SEALED TO CELL WITH WAX

STAINLESS STEEL CUP

FEP TEFLON

SOLID PLATIUM DISK (COUNTER ELECTRODE)

MICA WINDOW WITH SPUTTERED PLATINUM FILM (WORKING ELECTRODE)

FEP TEFLON

WINDOW SEALED BETWEEN RINGS WITH PYROCERAM

NICKEL-IRON ALLOY RING

PLATINUM RING

TUBE SEALED IN WITH EPOXY RESIN

2 MM PYREX CAPILLARY TUBE

FIGURE 5

ADSORPTION CELL WITH INLET AND OUTLET TUBES AND REFERENCE ELECTRODE

REFERENCE ELECTRODE
(MERCURY-MERCUROUS SULFATE)

STOPCOCK

PYREX

GRADED SEAL

SOFT GLASS BULB

RESERVOIR

Hg

Pt WIRE (ELECTRICAL CONNECTION TO REFERENCE ELECTRODE)

0.5mm CAPILLARY OUTLET TUBE

ELECTRICAL CONNECTION TO WORKING ELECTRODE (SPUTTERED Pt FILM)

COUNTERTUBE MOVES TO WINDOW

ADSORPTION CELL

ELECTRICAL CONNECTION TO COUNTER ELECTRODE

2mm CAPILLARY INLET TUBE

FIGURE 6

ADSORPTION CELL WITH MAGNETIC STIRRING
AND EXTERNAL COUNTER ELECTRODE

STOPCOCK

PT WIRE ELECTRICAL CONNECTION

PT GAUZE COUNTER ELECTRODE

REFERENCE ELECTRODE

ELECTRICAL CONNECTION TO WORKING ELECTRODE

1 MM CAPILLARY TUBES

RING-MICA WINDOW ASSEMBLY

MOTOR 100 RPM

BRASS SHAFT

PROPORTIONAL COUNTER TUBE MOVES TO WINDOW

ALNICO MAGNET

PYREX GLASS

WAX SEAL

GLASS-COVERED ALNICO MAGNET STIRRING BAR

FIGURE 7

STOCK SOLUTION STORAGE VESSEL

Labels in figure:
ARGON
MERCURY
10 cc HYPODERMIC SYRINGE
GLASS BEAD
STANDARD TAPER JOINT
ARGON
TEFLON STOPCOCK
TEFLON TUBE
CONSTRICTION
AQUEOUS SOLUTION OF RADIOACTIVE FUEL
MERCURY

FIGURE 8

EARLY ADSORPTION CELL USED FOR METHANOL ADSORPTION STUDIES

FIGURE 9

ADSORPTION OF RADIOMETHANOL ONTO 1000 Å THICK PLATINUM FILMS; 0.0005 MOLAL SOLUTIONS

ELECTROLYTE

○ PURE WATER
□ 0.025 MOLAL AQUEOUS KOH
△ 0.025 MOLAL AQUEOUS H₂SO₄

SOLUTION COUNT

* ZERO COUNTING RATE

APPARENT NUMBER OF MONOLAYERS

HOURS ELAPSED

FIGURE 10

ADSORPTION OF RADIO n-BUTANE FROM INH$_2$SO$_4$ ON TO A 2000 Å-THICK PLATINUM FILM AS A FUNCTION OF POTENTIAL

USING CELL OF FIGURE 5
O ANNEALED 450°C, 0.75 HRS.
□ ANNEALED 600°C, 2 HRS.

RADIO n-BUTANE ADSORBED, C/M

ELECTRODE POTENTIAL, VOLTS vs
Hg/Hg$_2$SO$_4$/1NH$_2$SO$_4$ + Hg$_2$SO$_4$ (SAT'D.)

FIGURE 11

LOSS OF RADIO n-BUTANE (IN IN H₂ SO₄) FROM ADSORPTION CELLS

FIGURE 12

ADSORPTION OF RADIO n-BUTANE FROM IN H_2SO_4 ON TO 2000 Å-THICK PLATINUM FILMS; ONE HOUR COUNTING TIME AT EACH POTENTIAL

FIGURE 13

ADSORPTION OF RADIO n-BUTANE FROM I N H_2SO_4 ON TO A 2000Å.—THICK PLATINUM FILM; SOLUTION UNSTIRRED; EQUILIBRIUM ADSORPTION AT EACH POTENTIAL

ELECTRODE POTENTIAL, VOLTS vs.
Hg / Hg_2SO_4 / IN H_2SO_4 + Hg_2SO_4 (SAT'D)

FIGURE 14

TIME DEPENDENCE OF ADSORPTION AND DESORPTION OF RADIO n-BUTANE AT SEVERAL ELECTRODE POTENTIALS; SOLUTION UNSTIRRED

FIGURE 15

INFRARED SPECTRA OF
METHANOL ON SILICA AEROGEL

O-H STRETCHING

AFTER D₂O EXCHANGE

ORIGINAL

FREQUENCY (cm⁻¹)

TRANSMISSION

C-H STRETCHING

ORIGINAL

O-D STRETCHING

AFTER D₂O
EXCHANGE

FREQUENCY (cm⁻¹)

TRANSMISSION

FIGURE 16

TOTAL INTERNAL REFLECTION FOR
STUDY OF ADSORPTION

(a) PATH OF LIGHT RAY IN TOTAL INTERNAL REFLECTION

(b) POSSIBLE USE OF INTERNAL REFLECTION TO STUDY
ADSORPTION (STACKED ELEMENTS IN CLOSE CONTACT)

FIGURE 17

MULTIPLE INTERNAL REFLECTION

POROUS PT. FILM

THIN GERMANIUM PLATE

I.R. RAY

FIGURE 18

STEARIC ACID ON GERMANIUM

FIGURE 19

INFRARED CELL FOR MULTIPLE INTERNAL REFLECTION STUDIES

LIQUID OR GAS CONNECTIONS

LENGTHS OF 1/4" O.D. STEEL TUBING THREADED TO BLOCK

HOLES (1/8" DIA.) DRILLED AS SHOWN CENTERED BETWEEN FRONT AND BACK

1cm

63 mm

STEEL BLOCK

SLOT (1MM WIDE) HOLDS GERMANIUM WAFER(S).

5mm

22mm

45°

40mm

(DRIFT PINS - NOT SHOWN - MAINTAIN ALIGNMENT OF THE TWO HALVES OF THE SPLIT BLOCK. HALVES CLAMPED AND/OR CEMENTED TOGETHER)

Ge WAFER

WAFER(S) HELD BETWEEN RUBBER, TEFLON OR AgCl GASKETS AND COMPRESSED IN CELL ABOVE. (WAFER EDGES DRY)

GASKETS (BOTH EDGES)

HOLE IF MORE THAN I WAFER

FIGURE 20

CAVITY, COILS AND ELECTROCHEMICAL CELL FOR ESR STUDIES

FIGURE 21

CELL FOR ELECTRON SPIN RESONANCE STUDIES OF ELECTRODES

MICROWAVE CAVITY

SAMPLE RESERVOIR

COUNTER ELECTRODE

WORKING ELECTRODE

TEFLON PLUG

TEFLON TAPE

FIGURE 22

EFFECT OF OXYGEN ON SIGNALS FROM ANODICALLY GENERATED FREE RADICALS IN AQUEOUS SOLUTION OF p-AMINO PHENOL AT pH 9.5

a. OXYGEN-FREE SOLUTION

b. EFFECT OF ADDED O_2

FIGURE 23

RELATIVE ESR SIGNAL INTENSITY vs pH FOR RADICALS FROM ANODIC OXIDATION OF p—AMINO PHENOL IN THE PRESENCE OF VARIOUS SUBSTANCES

FIGURE 24

BLOCK DIAGRAM FOR
DIFFERENTIAL CAPACITY MEASUREMENTS

FIGURE 25
CELL FOR DIFFERENTIAL CAPACITANCE MEASUREMENTS

GAS INLET — — GAS OUTLET

PRE-ELECTROLYSIS VESSEL

PLATINUM FOIL PRE-ELECTROLYSIS ELECTRODE

GAS INLET

FRITTED DISC

COOLANT OUTLET

GAS OUTLET

COOLANT INLET

TEST ELECTRODE ASSEMBLY

LUGGIN CAPILLARY-ARM

CELL

PLATINUM GAUZE POLARIZING ELECTRODE

SOLUTION OUTLET OR GAS INLET

TEFLON STIRRING BAR

REFERENCE ELECTRODE

FIGURE 26

ELECTRODE CAPACITY VS. POTENTIAL FOR A BRIGHT PLATINUM
ELECTRODE IN 1 M H₂SO₄ AT SEVERAL METHANOL CONCENTRATIONS

FIGURE 27

$\theta_{METHANOL}$ FROM CAPACITY-POTENTIAL DATA VS.

log CONCENTRATION OF METHANOL

FIGURE 28

θ METHANOL FROM CAPACITANCE MEASURMENTS VS. TIME AT CONSTANT POTENTIAL FOR A BRIGHT PLATINUM ELECTRODE IN IM H_2SO_4 AT SEVERAL METHANOL CONCENTRATIONS

SYMBOL	MOLES/LITER
○	0.0106
□	0.0170
◁	0.0318
▷	0.0424
●	0.0636
■	0.1380
◀	0.4030
▽	2.90

θ METHANOL

TIME, MINUTES

FIGURE 29

EXAMPLE OF TRIAL FIT BY COMPUTOR OF DATA FOR ADSORPTION OF
METHANOL IN IN H_2SO_4 AT BRIGHT PLATINUM AT 25° C
SOLID LINES EQUAL COMPUTOR SOLUTION FOR p = 1 AND q = 2
SYMBOLS EQUAL EXPERIMENTAL POINTS

CONCENTRATION MeOH M/l

□	0.138
△	0.0636
○	0.0318
×	0.0170
●	0.0106

EQUATION: $\dfrac{d\theta}{dt} = K_1 C^p (1-\theta)^q e^{-K_2\theta/RT}$

TIME, MINUTES

θ METHANOL

FIGURE 30

⊕ FORMIC ACID FROM CAPACITANCE MEASUREMENTS vs TIME FOR A BRIGHT PLATINUM ELECTRODE IN 1 M H_2SO_4 + 0.0057 M FORMIC ACID AT SEVERAL CONTROLLED ELECTRODE POTENTIALS

ELECTRODE POTENTIAL

- ○ − 0.5 VOLTS
- □ − 0.4 "
- ◁ − 0.3 "
- ● − 0.2 "
- ■ − 0.1 "
- ▲ 0.0 "

TIME, MINUTES

⊕ FORMIC ACID

FIGURE 31

$\Theta_{FORMIC\ ACID}$ FROM CAPACITANCE MEASUREMENTS vs TIME FOR A BRIGHT PLATINUM ELECTRODE IN 1M H_2SO_4 + 0.0057 M FORMIC ACID AT SEVERAL CONTROLLED ELECTRODE POTENTIALS

ELECTRODE
POTENTIAL

● − 0.2 VOLTS
○ − 0.1 "
▲ − 0.3 "
△ − 0.5 "

FIGURE 32

ELECTRODE CAPACITY VS. POTENTIAL FOR A BRIGHT PLATINUM ELECTRODE IN 1 M H_2SO_4 SATURATED WITH PROPENE + HELIUM MIXTURES

FIGURE 33

ELECTRODE CAPACITY vs POTENTIAL FOR A BRIGHT PLATINUM ELECTRODE IN 85% H_3PO_4 AND IN 85% H_3PO_4 SATURATED WITH PROPANE AT 140°C.

ARROWS INDICATE THE DIRECTION OF POTENTIAL CHANGE

―――― 85% H_3PO_4

― ― ― 85% H_3PO_4 SATURATED WITH PROPANE

ELECTRODE POTENTIAL, E, VOLTS vs $Hg/Hg_2SO_4/2N\ H_2SO_4 + Hg_2SO_4$ (SAT'D)

ELECTRODE CAPACITY, C, $\mu F/CM^2$

FIGURE 34
BLOCK DIAGRAM FOR AUXILIARY EQUIPMENT

FIGURE 35

ANODIC CURRENT VS. TIME AT -0.2 VOLTS FOR OXIDATION OF METHANOL

CONCENTRATION OF METHANOL   0.0424 MOLES/LITER
HORIZONTAL SENSITIVITY   2.0 SECONDS/CM
VERTICAL SENSITIVITY 1×10^{-5} AMPS/CM

FIGURE 36

ANODIC CURRENT VS. TIME AT-0.2 VOLTS AT SEVERAL CONCENTRATIONS OF METHANOL

No.	SYMBOL	CONC MeOH MOLES/LITER	$\left(\dfrac{\Delta i}{\Delta t^{-\frac{1}{2}}}\right)$ amp-sec$^{\frac{1}{2}}$ x10^5
1a	○	0.0106	1.71
1b	□	0.0212	3.06
1c	△	0.0424	4.77
1d	▽	0.0848	7.42

Y-axis: CURRENT, i, μa

X-axis: $t^{-\frac{1}{2}}$ SEC$^{-\frac{1}{2}}$

FIGURE 37

ANODIC CURRENT VS. TIME AT -0.1 VOLTS AT SEVERAL CONCENTRATIONS OF METHANOL

No.	SYMBOL	CONC. MeOH MOLES/LITER	$\left(\dfrac{\Delta i}{\Delta t^{-\frac{1}{2}}}\right)$ amp-sec$^{\frac{1}{2}}$ $\times 10^{5}$
2a	△	0.0106	4.84
2b	▽	0.0212	9.83
2c	○	0.0424	14.30
2d	□	0.0848	19.50

FIGURE 38

ANODIC CURRENT VS. TIME AT O.O VOLTS AT SEVERAL CONCENTRATIONS OF METHANOL

250

3e

200

3d

CURRENT, I, μa

150

3c

100

No	SYMBOL	CONC MeOH MOLES/LITER	$\left(\dfrac{\Delta I}{\Delta t^{-\frac{1}{2}}}\right)$ amp-sec$^{\frac{1}{2}}$ x10^6
3c	○	0.0424	8.22
3d	□	0.0848	21.43
3c	△	0.1380	42.12

50

0   0.1   0.2   0.3   0.4   0.5   0.6   0.7   0.8   0.9   1.0

$t^{-\frac{1}{2}}$, SEC$^{-\frac{1}{2}}$

FIGURE 39

LOG SLOPE (i vs. $t^{-\frac{1}{2}}$) CURVES VS. LOG CONCENTRATION OF METHANOL AT SEVERAL ELECTRODE POTENTIALS

SYMBOL	ELECTRODE POTENTIAL	$\Delta LOG\left(\dfrac{\Delta i}{\Delta t^{-\frac{1}{2}}}\right)\Big/\Delta LOG$ CONC. MeOH
◯	- 0.2	0.630
△	- 0.1	0.512
▢	0.0	1.370

SLOPE OF i vs. $t^{-\frac{1}{2}}$ CURVES, AMPS/SEC.$^{-\frac{1}{2}}$

CONC. MeOH, MOLES/LITER

FIGURE 40

MAXIMUM ANODIC CURRENTS IN CURRENT-TIME CURVES VS.
CONCENTRATION OF METHANOL TAKEN AT VARIOUS POTENTIALS

FIGURE 42

ETHYLENE AT BRIGHT PLATINUM
CURRENT-TIME CURVES AT CONSTANT POTENTIAL AFTER
PRETREATMENT AT O_2 EVOLUTION

CONTROLLED POTENTIAL
— 0.0v
—·— -0.1v
—··— -0.2v
········ -0.3v
— —— +0.1v
········ +0.3v

ETHYLENE BRIGHT PT IM H_2SO_4 80°C
PRETREAT=1 MIN AT 1.2v

TIME, SECONDS

CURRENT, MILLIAMPS

ANODIC
CATHODIC

FIGURE 43

CURRENT VS. ELECTRODE POTENTIAL DURING POTENTIAL SWEEP ON A BRIGHT PLATINUM ELECTRODE IN IM H_2SO_4 + HYDROCARBON AT 80°C.

FIGURE 44

CURRENT VS. ELECTRODE POTENTIAL DURING POTENTIAL SWEEP ON A BRIGHT PLATINUM ELECTRODE IN IM H_2SO_4 + HYDROCARBON AT 80°C.

ELECTRODE POTENTIAL,E,VOLTS vs
$Hg/Hg_2SO_4/2N\ H_2SO_4+Hg_2SO_4(SAT'D)$

FIGURE 45

POTENTIAL SWEEPS OF ETHANE AND HELIUM
AT BRIGHT PLATINUM IN I M H_2SO_4 AT 80°C

SWEEP RATE = 17 MV/SEC.

FIGURE 46

POTENTIAL SWEEPS AT BRIGHT PLATINUM IN IM H_2SO_4 AT 80°C

SWEEP RATE = 17 MV/SEC.

FIGURE 47

POTENTIAL SWEEPS AFTER CATHODIC PRETREATMENT
AT BRIGHT PLATINUM IN I M H₂SO₄ AT 80°C

FIGURE 48

POTENTIAL SWEEPS AFTER ANODIC PRETREATMENT AT BRIGHT PLATINUM IN IM H_2SO_4 AT 80°C

PRETREAT = 5 MIN. AT + 1.2 V
SWEEP RATE = 8 MV/SEC.

R = REVERSAL OF SWEEP DIRECTION

ELECTRODE POTENTIAL, E, VOLTS vs $Hg/Hg_2SO_4/2N H_2SO_4 + Hg_2SO_4$(SAT'D)

FIGURE 49

COMPARISON OF FUEL OXIDATION CURRENTS
AFTER ANODIC AND CATHODIC PRETREATMENTS

——— ANODIC PRETREAT (FROM FIG. 48)

·········· CATHODIC PRETREAT (FROM FIG. 47)

FIGURE 50
BLOCK DIAGRAM OF X-Y PULSED POLARIZATION APPARATUS

UNCLASSIFIED